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THE EFFECT OF NON_RIGIDITY ON THE LINE STRENGTHS OF VIBRATIONAL-ROTATIONAL TRANSITIONS*

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Abstract

The effect of the difference in asymmetry of the ground and excited states of a vibrational band on the line strengths of the vibrational-rotational transitions has been investigated. It is found that for sufficiently large $\Delta\kappa$ ($\sim$.1-.2) in A and C type bands there is an enhancement of the line strengths of either the R or P branch, depending on whether κ of the ground state is greater or less than κ of the excited state. In B type bands certain sub-bands are enhanced, but in general no branch of the band is enhanced as a whole.

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Introduction

In the early analyses of the rotational fine structure of vibrational bands of asymmetric rotors, the intensities of the fine structure components were estimated from the intensities of the transitions in the closer symmetric limit. Cross, Hainer and King[1] have shown that such a procedure is dangerous.

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[1] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. 12, 210 (1944).

CHK have published a very useful table of line strengths for the rigid asymmetric rotor. It is well known, however, that molecules are not rigid rotors. In fact, in those cases where complete analyses of the rotational-fine structure have been made, it has been necessary to use effective moments of inertia for each vibrational state. This difference of asymmetry in the two vibrational states, the asymmetry being measured by $\kappa = (2b-a-c)/(a+c)$,[2] can have marked effect on

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[2] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. 11, 27 (1943).

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the line strengths of various transitions if $\Delta\kappa$ between the two vibrational states is large. If $\Delta\kappa$ is small, then the line strengths calculated for the rigid approximation are sufficient. However, for some of the higher combination bands of light molecules such as water and hydrogen sulfide $\Delta\kappa$ can be as large as .1 or .2 and in free radical spectra even larger changes can occur.[3]

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[3] This was kindly pointed out by Dr. Herzberg at the "Symposium on Molecular Structure and Spectroscopy," Columbus, Ohio, 1953.

In these cases the intensity pattern calculated for the rigid approximation breaks down.

Theory

The problem of the asymmetric rotor has been treated in great detail.[1,2] In setting up the energy matrix, Wang combinations of symmetric rotor wave functions must be used.[2] Then an orthonormal transformation can be found which diagonalizes the energy, i.e., such that

$$E(\kappa) = T' \, X' \, E \, X \, T, \tag{1}$$

where X is defined as reference 2, equation 29, and serves to give the Wang combinations of the symmetric rotor wave functions, and T is the transformation which diagonalizes the energy matrix.

The line strengths are obtained by squaring the matrix elements of the direction cosine matrix of the asymmetric rotor. If the direction cosine matrix is also set up in terms of symmetric rotor wave functions, then the asymmetric rotor direction cosine matrix is obtained by[1]

$$\Phi_{Fg}^{A} = T_1' \, X' \, \Phi \, X \, T_2, \tag{2}$$

where T_1 and T_2 are the transformations which diagonalize the ground and excited states respectively. The case where $T_1 = T_2 = T$ was considered by Cross, Hainer and King. In this paper the case will be considered where $T_1 \neq T_2$.

The transformations for $\kappa = .5$ and $\kappa = 1$ have been evaluated up through $J = 4$ and applied to the direction cosine matrix in the order

$$\Phi_{Fg}^{A} = T\,(.5) \, X' \, \Phi \, X \, T(1) \tag{3}$$

This order assumes that $\kappa = .5$ in the ground state and $\kappa = 1$ in the excited state. A change this large is likely to be encountered only in the case of free radical spectra, but the large change was used in order to emphasize any regularities which might appear. The resulting elements were squared and multiplied by 10^4 in order to be consistent with reference 1. The transitions were then sorted into sub-branches in order to find any regularities which occurred.

Discussion

The regularities found are summarized in Table I. It was found necessary to consider two cases; (1) κ of ground state less than κ in the excited state, and (2) κ of ground state greater than κ in the excited state. The conclusions for case 2 are the converse of the conclusions for case 1, so only case 1 will be discussed.

The most striking regularities are found in the A and C type bands, i.e., the dipole moment change along the least and largest inertial axes respectively. In the A type band it is found that the P branch line strengths are enhanced, quite generally, with respect to the R branch, while in the C type bands it is the R branch which is enhanced. Certain of the Q branch sub-bands are also enhanced under these conditions.

An inspection of the table of line strengths in reference 1 shows that it is not always necessary to consider the difference of asymmetry of the two vibrational states. For an A type band, the change of line strength with κ is very small in the region $-1 \leq \kappa \leq 0$. Hence a $\Delta\kappa$ in this region would not lead to pronounced effects. However, for $0 \leq \kappa \leq 1$ the change in line strength with κ is quite steep; hence in this region of κ one might expect quite pronounced effects. For C type bands the pronounced effects are to be expected in the region $-1 \leq \kappa \leq 0$. The line strengths of Q branch transitions have a much greater κ dependence than either the P or R branch transitions. Such unexpected intensity patterns as can arise from these Q branch transitions could become a useful tool in the analysis of vibrational-rotational bands.

In B type bands, i.e. the dipole moment change along the intermediate inertial axis, no particular branch is generally enhanced. It is found that certain sub-bands in the P, Q and R branches are enhanced. It is again to be hoped that the intensity patterns found in this special case of large $\Delta\mathcal{H}$ will become a useful analytical tool. In order to give some idea of the size of these effects, in Table II are shown the calculated line strengths for the main sub-bands for both A and B type selection rules through J = 4. No C type examples are given for the effect is very small in the $\mathcal{H}$ region chosen, as pointed out earlier. A ground state of 0.5 and an excited state $\mathcal{H}$ of 0.7 have been used in the calculations. The line strengths for the rigid approximations in which $\mathcal{H}$ = 0.5 and 1.0 have been included for comparison.

In many instances these effects are small, of the order of 1 or 2% for a $\Delta\mathcal{H}$ = .2. However, for many Q branch transitions in the appropriate $\mathcal{H}$ range these effects can be as much as 10% even at low J. In the case of free radicals[4] where $\Delta\mathcal{H}$ may be as high as 0.6 - 0.8 then these effects will be pronounced in practically all transitions.

[4] D. A. Ramsay, Private communication.

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Table I

	$\mathcal{H}_G < \mathcal{H}_e$				$\mathcal{H}_e < \mathcal{H}_G$			
Stronger	${}^{be}R_{1,1}$	${}^{be}P_{\bar{1},1}$	${}^{be}Q_{1,\bar{1}}$	${}^{bo}Q_{1.\bar{1}}$	${}^{bo}R_{1,\bar{1}}$	${}^{bo}P_{\bar{1},1}$	${}^{ae}R_{0\bar{1}}$	${}^{ao}R_{01}$
sub-band	${}^{ae}P_{0,\bar{1}}$	${}^{ao}P_{0,\bar{1}}$	${}^{ae}Q_{0,\bar{1}}$	${}^{ao}Q_{\bar{2},1}$	${}^{be}Q_{\bar{1},1}$	${}^{bo}Q_{\bar{1},1}$	${}^{ao}Q_{0,\bar{1}}$	${}^{ae}Q_{2,\bar{1}}$
	${}^{co}Q_{\bar{1},0}$	${}^{ce}Q_{\bar{1},2}$	${}^{ce}R_{1,0}$	${}^{co}R_{1,0}$	${}^{ce}Q_{1,0}$	${}^{co}Q_{1,\bar{2}}$	${}^{co}P_{\bar{1},0}$	${}^{co}P_{\bar{1},0}$

$\mathcal{H}_G$ = ground state

$\mathcal{H}_e$ = excited state

Sub-band labelling is that suggested in reference 1.

Table II

A type Band

	$^{ae}Q_{01}$				$^{ao}Q_{0\bar{1}}$		
Transition	$s^2(1)$	$s^2(.5\text{-}7)$	$s^2(.5)$	Transition	$s^2(1)$	$s^2(.5\text{-}7)$	$s^2(.5)$
$1_1 - 1_0$	15000	15000	15000	$1_0 - 1_1$	15000	15000	15000
$2_2 - 2_1$	25000	28223	28223	$2_1 - 2_2$	25000	26926	28223
$3_3 - 3_2$	35000	44966	45104	$3_2 - 3_3$	35000	41498	45104
$4_4 - 4_3$	45000	63926	64494	$4_3 - 4_4$	45000	58949	64494
$2_0 - 2_{-1}$	8333	8333	8333	$2_{-1} - 2_0$	8333	8333	8333
$3_1 - 3_0$	14583	16278	16278	$3_0 - 3_1$	14583	15514	16278
$4_2 - 4_1$	20250	26100	26168	$4_1 - 4_2$	20250	23431	26168
$3_{-1} - 3_{-2}$	8750	7730	7403	$3_{-2} - 3_{-1}$	8750	7505	7403
$4_0 - 4_{-1}$	15750	13893	13221	$4_{-1} - 4_0$	15750	12987	13221
$4_{-2} - 4_{-3}$	9000	8087	7587	$4_{-3} - 4_{-2}$	9000	7616	7587

	$^{ae}Q_{2\bar{1}}$				$^{ao}Q_{\bar{2}1}$		
$2_{-2} - 2_1$	8333	5110	5110	$2_1 - 2_{-2}$	8333	6405	5110
$3_{-1} - 3_2$	14583	5395	5722	$3_2 - 3_{-1}$	14583	9328	5722
$4_0 - 4_3$	20250	3691	4363	$4_3 - 4_0$	20250	9896	4363
$3_{-3} - 3_0$	8750	7055	7055	$3_0 - 3_{-3}$	8750	7819	7055
$4_{-2} - 4_1$	15750	10714	11214	$4_1 - 4_{-2}$	15750	13952	11214
$4_{-4} - 4_{-1}$	9000	7565	7558	$4_{-1} - 4_{-4}$	9000	8138	7558

Table II (cont.)

Transition	$^{ae}R_{01}$ $S^2(1)$	$S^2(.5\text{-}7)$	$S^2(.5)$	Transition	$^{ae}P_{0\bar{1}}$ $S^2(1)$	$S^2(.5\text{-}7)$	$S^2(.5)$
$0_0 - 1_{-1}$	10000	10000	10000	$1_{-1} - 0_0$	10000	10000	10000
$1_{-1} - 2_{-2}$	15000	16159	16934	$2_{-2} - 1_{-1}$	15000	16934	16934
$2_{-2} - 3_{-3}$	25000	25351	25893	$3_{-3} - 2_{-2}$	25000	25968	25893
$3_{-3} - 4_{-4}$	35000	35373	35773	$4_{-4} - 3_{-3}$	35000	35793	35773
$1_1 - 2_0$	15000	15000	15000	$2_0 - 1_1$	15000	15000	15000
$2_0 - 3_{-1}$	16667	20381	22500	$3_{-1} - 2_0$	16667	22500	22500
$3_{-1} - 4_{-2}$	26250	27225	29261	$4_{-2} - 3_{-1}$	26250	29554	29261
$2_2 - 3_1$	20000	18530	18636	$3_1 - 2_2$	20000	19229	18636
$3_1 - 4_0$	18750	25684	29055	$4_0 - 3_1$	18750	29431	29055
$3_3 - 4_2$	25000	19832	20331	$4_2 - 3_3$	25000	22214	20331
	$^{ao}R_{01}$				$^{ao}P_{0\bar{1}}$		
$1_0 - 2_{-1}$	15000	15000	15000	$2_{-1} - 1_0$	15000	15000	15000
$2_{-1} - 3_{-2}$	25000	25445	25710	$3_{-2} - 2_{-1}$	25000	25710	25710
$3_{-2} - 4_{-3}$	35000	35406	35758	$4_{-3} - 3_{-2}$	35000	35765	35758
$2_1 - 3_0$	16667	16667	16667	$3_0 - 2_1$	16667	16667	16667
$3_0 - 4_{-1}$	26250	27566	28252	$4_{-1} - 3_0$	26250	28258	28252
$3_2 - 4_1$	18750	18171	18207	$4_1 - 3_2$	18750	18414	18207

Table II (cont.)

Transition	$s^2(1)$	$s^2(.5-7)$	$s^2(.5)$	Transition	$s^2(1)$	$s^2(.5-7)$	$s^2(.5)$
$^{be}Q_{1,\bar{1}}$				$^{be}Q_{\bar{1},1}$			
$1_{-1} - 1_1$	15000	15000	15000	$1_1 - 1_{-1}$	15000	15000	15000
$2_0 - 2_2$	25000	22912	21289	$2_2 - 2_0$	25000	21289	21289
$3_1 - 3_3$	35000	27961	23196	$3_3 - 3_1$	35000	23041	23196
$4_2 - 4_4$	45000	29930	22157	$4_4 - 4_2$	45000	21541	22157
$2_{-2} - 2_0$	8333	12044	12044	$2_0 - 2_{-2}$	8333	10422	12044
$3_{-1} - 3_1$	14583	25529	24417	$3_{-1} - 3_1$	14583	19652	24417
$4_0 - 4_2$	20250	40243	36119	$4_2 - 4_0$	20250	28245	36119
$3_{-3} - 3_{-1}$	8750	11750	10583	$3_{-1} - 3_{-3}$	8750	9471	10583
$4_2 - 4_0$	15750	21904	20622	$4_0 - 4_{-2}$	15750	16498	20622
$4_{-4} - 4_{-2}$	9000	10655	10617	$4 - 4$	9000	9776	10544
$^{bo}Q_{1,\bar{1}}$				$^{bo}Q_{\bar{1},1}$			
$2_{-1} - 2_1$	8333	8333	8333	$2_1 - 2_{-1}$	8333	8333	8333
$3_0 - 3_2$	14583	14583	13160	$3_2 - 3_0$	14583	13160	13160
$4_1 - 4_3$	20250	20171	16126	$4_3 - 4_1$	20250	16092	16126
$3_{-2} - 3_0$	8750	10173	10173	$3_0 - 3_{-2}$	8750	9592	10173
$4_{-1} - 4_1$	15750	19977	18280	$4_1 - 4_{-1}$	15750	16716	18280
$4_{-3} - 4_{-1}$	9000	10515	10584	$4_{-1} - 4_{-3}$	9000	9839	10584

Table II (cont.)

Transition	bo $R_{1,1}$ $s^2(1)$	$s^2(.5\text{-}7)$	$s^2(.5)$	Transition	bo $P_{\bar{1},1}$ $s^2(1)$	$s^2(.5\text{-}7)$	$s^2(.5)$
$0_0 - 1_0$	10000	10000	10000	$1_0 - 0_0$	10000	10000	10000
$1_{-1} - 2_{-1}$	15000	15000	15000	$2_{-1} - 1_{-1}$	15000	15000	15000
$2_{-2} - 3_{-2}$	25000	24330	24086	$3_{-2} - 2_{-2}$	25000	24183	24086
$3_{-3} - 4_{-3}$	35000	34421	34083	$4_{-3} - 3_{-3}$	35000	34114	34083
$1_1 - 2_1$	15000	15000	15000	$2_1 - 1_1$	15000	15000	15000
$2_0 - 3_0$	16667	16667	16667	$3_0 - 2_0$	16667	16667	16667
$3_{-1} - 4_{-1}$	26250	24034	23550	$4_{-1} - 3_{-1}$	26250	23941	23550
$2_2 - 3_2$	20000	21295	21383	$3_2 - 2_2$	20000	20414	21383
$3_1 - 4_1$	18750	19506	19563	$4_1 - 3_1$	18750	19182	19563
$3_3 - 4_3$	25000	29205	29580	$4_3 - 3_3$	25000	27992	29580
	bo $R_{1,\bar{1}}$				be $P_{\bar{1},1}$		
$1_0 - 2_2$	5000	6253	7226	$2_2 - 1_0$	5000	7226	7226
$2_1 - 3_3$	10000	14021	16667	$3_3 - 2_1$	10000	16667	16667
$3_2 - 4_4$	15000	23369	27406	$4_4 - 3_2$	15000	27337	27406
$2_{-1} - 3_1$	1667	2245	2792	$3_1 - 2_{-1}$	1667	2792	2792
$3_0 - 4_2$	3750	5675	7602	$4_2 - 3_0$	3750	7602	7602
$3_{-2} - 4_0$	1250	1185	1537	$4_0 - 3_{-2}$	1250	1705	1537